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Tailored Magnetic Properties in Trinuclear Copper(II) Complexes: Synthesis, Structure, and Magnetic Properties of Complexes Derived from [1,3-Propanediylbis(oxamato)]cuprate(II) ($[Cu(pba)]^{2-}$)

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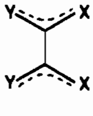
Five new trinuclear Cu(II) complexes were synthesized: $\{[(tmen)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2$ (**1**), $\{[(pet)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2\cdot{}^1/_2H_2O$ (**2**), $\{[(pmd)Cu]_2[\mu\text{-}Cu(pba)]\}(BPh_4)_2\cdot CH_3CN$ (**3**), $\{[(bapa)Cu]_2[\mu\text{-}Cu(pba)(H_2O)]\}(PF_6)_2$ (**4**), and $\{[(terpy)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2$ (**5**), where Cu(pba) = [1,3-propanediylbis(oxamato)]cuprate(II), tmen = *N,N,N′,N′*-tetramethylethylenediamine, pet = *N,N,N′,N″,N″*-pentaethyldiethylenetriamine, pmd = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, bapa = bis(3-aminopropyl)amine, and terpy = 2,2′:6′,2″-terpyridine. The structures of **1**–**4** were determined by X-ray analysis. The crystals of **1** are orthorhombic, space group $Pn2_1a$, with $a = 26.529(3)$ Å, $b = 14.077(2)$ Å, $c = 8.330(1)$ Å, $Z = 4$, and $R = 0.047$ for 1804 reflections observed. The crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 20.070(6)$ Å, $b = 17.430(5)$ Å, $c = 15.334(4)$ Å, $\alpha = 91.06(2)°$, $\beta = 110.88(2)°$, $\gamma = 91.54(2)°$, $Z = 4$, and $R = 0.108$ for 3701 reflections observed. The crystals of **3** are monoclinic, space group $P2_1/n$, with $a = 12.127(1)$ Å, $b = 35.447(5)$ Å, $c = 17.112(2)$ Å, $\beta = 95.72(1)°$, $Z = 4$, and $R = 0.045$ for 4879 reflections observed. The crystals of **4** are orthorhombic, space group *Pbca*, with $a = 38.797(4)$ Å, $b = 16.938(3)$ Å, $c = 11.139(2)$ Å, $Z = 8$, and $R = 0.059$ for 1804 reflections observed. In **1** the three copper(II) ions are all approximately square-planar with almost coplanar basal planes. The central copper(II) ions of **2** and **4** are square-pyramidal, the apical positions being occupied by a perchlorate and a water oxygen, respectively. In **3** the central copper ion is square-planar. The terminal copper ions of compounds **2**–**4** are all pentacoordinated with geometries that are intermediate between square-pyramidal and trigonal-bipyramidal. If the coordination is described in terms of square-pyramidal geometry, the basal plane of each terminal copper is approximately perpendicular to the basal plane of the central copper ion. The distortion toward trigonal-bipyramidal geometry is largest for compound **2** and smallest for **4**. Magnetic susceptibility and EPR measurements have been carried out for this series of complexes. The magnetic data have been interpreted using the Heisenberg Hamiltonian and lead to J values equal to −360, −170, −153, −110, and −80 cm^{-1} for **1**–**5**, respectively. The intensity of the magnetic coupling is discussed in relation to the relative orientation of magnetic orbitals. The symmetry of EPR spectra is also discussed.

Introduction

Magneto–structural correlations in molecular species have been investigated over a large number of binuclear copper(II) systems.[1–5] It is now well established that $C_2X_2Y_2^{2-}$ (X, Y = O, N, S) ligands are very efficient in propagating the magnetic interaction when they bridge two metal centers.



X, Y = O, N, S

It has been shown in binuclear systems that it is possible to tune the magnitude of the interaction by retaining the same bridging ligand and changing only the terminal ones.[2c,3d] In comparison, the literature on magnetic properties of trinuclear

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Table I. Summary of Experimental Crystal Data for the X-ray Diffraction Studies on Compounds 1–4

	compound			
	1	**2**	**3**	**4**
formula	$C_{19}H_{38}Cl_2Cu_3N_6O_{14}$	$C_{35}H_{77}Cl_2Cu_3N_8O_{14}\cdot1/2H_2O$	$C_{73}H_{92}B_2Cu_3N_8O_6\cdot CH_3CN$	$C_{19}H_{42}Cu_3F_{12}N_8O_7P_2$
fw	836.09	1099.56	1430.9	975.14
space group	$Pn2_1a$	$P1$	$P2_1/n$	$Pbca$
a (Å)	26.529(3)	20.070(6)	12.127(1)	38.797(4)
b (Å)	14.077(2)	17.430(5)	35.447(5)	16.938(3)
c (Å)	8.330(1)	15.334(4)	17.112(2)	11.139(2)
α (deg)	90.0	91.06(2)	90.0	90.0
β (deg)	90.0	110.88(2)	95.72(1)	90.0
γ (deg)	90.0	91.54(2)	90.0	90.0
V (Å^3)	3111(1)	5008(4)	7319(3)	7320(3)
Z	4	4	4	8
T (°C)	25	25	20	25
ρ_{calcd} (g cm^{-3})	1.725	1.458	1.299	1.751
μ(Mo Kα)(cm^{-1})	23.51	14.86	9.20	19.97
transm coeff	1	1	0.95–0.78	1
$R(F_o)$,[a] $R_w(F_o)$[b]	0.047, 0.051	0.108, 0.113	0.045, 0.043	0.059, 0.063
radiation (λ, Å)	Mo Kα (0.710 69)			

[a] $R(F_o) = \sum||F_o| - |F_c||^2/\sum|F_o|$. [b] $R_w(F_o) = \sum w||F_o| - |F_c||^2/\sum w|F_o|$.

systems is rather limited.[6] We have recently studied the influence of terminal ligands on the amplitude of the magnetic exchange interaction through the oxamato bridge in trinuclear complexes.[7] Since structural data were not available, magneto–structural correlations were assumed.

In this paper we present the study of five new trinuclear compounds, four of which were structurally characterized: $\{[(tmen)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2$ (**1**), $\{[(pet)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2\cdot{}^1/_2H_2O$ (**2**), $\{[(pmd)Cu]_2[\mu\text{-}Cu(pba)]\}(BPh_4)_2\cdot CH_3CN$ (**3**), $\{[(bapa)Cu]_2[\mu\text{-}Cu(pba)(H_2O)]\}(PF_6)_2$ (**4**), and $\{[(terpy)Cu]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2$ (**5**) with Cu(pba) = [1,3-propanediylbis(oxamato)]cuprate(II), tmen = *N,N,N′,N′*-tetramethylethylenediamine, pet = *N,N,N′,N″,N″*-pentaethyldiethylenetriamine, pmd = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, bapa = bis(3-aminopropyl)amine, and terpy = 2,2′:6′,2″-terpyridine.

Experimental Section

Synthesis. *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Preparation of the Copper(II) Complexes. The syntheses of sodium [propanediylbis(oxamato)]cuprate(II) hexahydrate[8] ($Na_2[Cu(pba)]\cdot6H_2O$) and copper(II) trifluoromethanesulfonate[9] ($Cu(CF_3SO_3)_2$) were carried out according to the literature methods.

$[\{(tmen)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2$ (1). A 116-mg amount (1 mmol) of tmen (*N,N,N′,N′*-tetramethylethylenediamine) was added dropwise with stirring to 0.37 g (1 mmol) of copper(II) perchlorate hexahydrate dissolved in 10 mL of water. The solution turned dark blue. After some minutes, a hot solution of 0.22 g (0.5 mmol) of $Na_2[Cu(pba)]\cdot6H_2O$ in 10 mL of water was added slowly to the stirred solution. The resulting green mixture was left to stand until dark green crystals of the complex were formed. The product was recrystallized in acetonitrile. Anal. Calcd for $[\{(tmen)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2$, $C_{19}H_{38}Cl_2Cu_3N_6O_{14}$: C, 27.29; H, 4.58; Cl, 8.48; Cu, 22.80; N, 10.05. Found: C, 27.2; H, 4.4; Cl, 8.1; Cu, 22.6; N, 10.0.

$[\{(pet)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2\cdot{}^1/_2H_2O$ (2). A 243-mg amount (1 mmol) of *N,N,N′,N″,N″*-pentaethyldiethylenetriamine (pet) was added dropwise to a stirred hot solution of 0.38 g of copper(II) trifluoromethanesulfonate in 10 mL of water. To the filtered blue solution was added 10 mL of hot water containing 0.22 g (0,5 mmol) of $Na_2[Cu(pba)]\cdot6H_2O$. When the solution turned green, 0.18 g (1.25 mmol) of sodium perchlorate monohydrate dissolved in 5 mL of water was further added. A green precipitate immediately formed, which was collected by filtration, washed with water, and recrystallized in acetonitrile. Anal. Calcd for $[\{(pet)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2$, $C_{35}H_{72}Cl_2Cu_3N_8O_{14}\cdot{}^1/_2H_2O$: C, 38.23; H, 6.69; Cl, 6.45; Cu, 17.34; N, 10.19. Found: C, 38.2; H, 6.9; Cl, 6.2; Cu, 17.2; N, 10.2.

$[\{(pmd)Cu\}_2\{\mu\text{-}Cu(pba)\}](BPh_4)_2\cdot CH_3CN$ (3). An aqueous solution of 0.35 g (2 mmol) of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmd) was added to 15 cm^3 of an aqueous solution of 0.76 g (2 mmol) of $Cu(CF_3SO_3)_2$. The blue solution was stirred at room temperature and filtered. An aqueous solution of 0.44 g (1 mmol) of $Na_2[Cu(pba)]\cdot6H_2O$ was added with constant stirring. No precipitate formed. A 20-cm^3 volume of an aqueous solution of 0.68 g (2 mmol) of $NaBPh_4$ was subsequently added with vigorous stirring. A light green precipitate immediately formed; it was separated by filtration, washed with abundant water, and dried over P_2O_5. After this powder was dissolved in acetonitrile and the resultant mixture was filtered to eliminate any impurity, the solution was left to stand at room temperature. After several days well-formed, blue crystals of **3** had grown. Neither IR spectrum nor elementary analysis of powdered samples showed the presence of the cocrystallized acetonitrile molecule detected in the X-ray analysis. Anal. Calcd for $[\{(pmd)Cu\}_2\{\mu\text{-}Cu(pba)\}](BPh_4)_2$, $C_{73}H_{92}B_2Cu_3N_8O_6$: C, 63.09; H, 6.67; Cu, 13.72; N, 8.06. Found: C, 62.9; H, 6.7; Cu, 13.6; N, 8.1.

$[\{(bapa)Cu\}_2\{\mu\text{-}Cu(pba)(H_2O)\}](PF_6)_2$ (4). A solution of 0.38 g (1 mmol) of copper(II) trifluoromethanesulfonate in 10 mL of water was prepared, and 131 mg of bapa (bis(3-aminopropyl)amine) was added with stirring to produce a blue solution. A hot solution of 0.22 g (0.5 mmol) of $Na_2[Cu(pba)]\cdot6H_2O$ in 10 mL of water was added dropwise, resulting in an intense green color. An excess (0.25 g, 1.36 mmol) of potassium hexafluorophosphate dissolved in the minimum amount of water was added. After some minutes, a green precipitate of **4** was formed and collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the remaining solution. Anal. Calcd for $[\{(bapa)Cu\}_2\{\mu\text{-}Cu(pba)(H_2O)\}](PF_6)_2$, $C_{19}H_{42}Cu_3F_{12}N_8O_7P_2$: C, 23.40; H, 4.34; Cu, 19.55; N, 11.49. Found: C, 23.3; H, 4.4; Cu, 19.4; N, 11.4.

$[\{(terpy)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2$ (5). A 0.233-g amount (1 mmol) of terpy (2,2′:6′,2″-terpyridine) were dissolved in a boiling mixture of 2:1 methanol–water. Furthermore, a methanolic solution (5 mL) containing 0.370 g (1 mmol) of copper(II) perchlorate hexahydrate was added, resulting in a green mixture. Finally, 15 mL of a hot aqueous solution containing 0.22 g (0.5 mmol) of $Na_2[Cu(pba)]$ hexahydrate was added dropwise to the boiling mixture. A green precipitate formed immediately. The product **5** was collected quantitatively and dried over P_2O_5. Anal. Calcd for $[\{(terpy)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2$, $C_{37}H_{28}Cl_2Cu_3N_8O_{14}$: C, 41.53; H, 2.64; Cl, 6.63; Cu, 17.81; N, 10.47. Found: C, 41.6; H, 2.6; Cl, 6.4; Cu, 17.9; N, 10.4.

X-ray Data Collection and Structure Determination. Crystal data and refinement results for each compound are summarized in Table I.

Data for compounds **1**, **2**, and **4** were collected on a Philips PW-1100 diffractometer and for compound **3** on a CAD4 instrument, using

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monochromatic Mo Kα radiation. Unit cell parameters were determined from 25 automatically centered reflections in the θ-ranges 8–12° (compounds **1**, **2**, **4**) and 8–19° (compound **3**). Intensity data were collected in the θ-ranges 2–25° (compounds **1**, **2**, **4**) and 2–22.5° (compound **3**), with the ω-scan technique. The total number of unique reflections recorded was 2312, 6231, 9523, and 2164 for compounds **1**–**4**, respectively. In each case the three reference reflections monitored throughout the data collection showed no significant intensity decay. The data were corrected for Lorentz and polarization effects. For compound **3** an absorption correction was applied, using the Gaussian integration method.

Structures **1** and **2** were solved by Patterson syntheses, and structures **3** and **4** by direct methods. Refinements were performed by least-squares methods minimizing the function $\sum w||F_o| - |F_c||^2$, with $w = [\sigma^2(F_o) + 0.0037|F_o|^2]^{-1}$ in the case of compounds **1**, **2**, and **4** and with $w = 4F_o^2[\sigma_c^2 + (0.02F_o^2)^2]^{-1}$ in the case of compound **3**. For compounds **1**, **2**, and **4**, the calculations were carried out with the SHELX76[10] and SHELXS[11] computer programs; for compound **3** calculations were carried out with the Enraf-Nonius structure determination programs.[12] Atomic scattering factors with anomalous dispersion terms included were those of Cromer and Mann.[13] Special aspects of solution and refinement of each structure are described separately in the following paragraphs.

Compound 1. The space group is not unambiguously determined by the systematic extinctions, but a noncentrosymmetric cell was assumed on the basis of the intensity distribution. This assumption was confirmed by the successful solution and refinement. One of the perchlorate ions is disordered. For two of the oxygen atoms two positions were found, and occupancy factors of 0.5 were assumed according to the height of peaks observed in the Fourier synthesis. Non-H atoms were refined anisotropically, and H atoms isotropically. All hydrogen atoms were included at calculated positions with an overall isotropic temperature factor. Assuming a riding model, their positions were adjusted in the same way as those of the atoms to which they are bonded. A total of 417 parameters were refined in the full-matrix least-squares refinement, which included 1804 reflections with $I \geq 2.5\sigma(I)$. The final $R = 0.047$ and $R_w = 0.051$, with maximum shift/esd. = 0.1. The maximum and minimum peaks found in the difference synthesis were 0.3 and –0.3 e Å^{-3}, respectively.

Compound 2. Only 3701 reflections fulfilled the condition $I \geq 2.5\sigma(I)$. As there are two molecules in the asymmetric unit, the ratio of the number of observations to the number of parameters is low; hence, the perchlorate and water oxygen atoms were refined isotropically and hydrogen atoms were not included. Least-squares refinement which was performed with three blocks containing 469, 469, and 105 parameters, respectively, converged at $R = 0.108$ and $R_w = 0.113$, with maximum shift/esd = 0.1. The maximum and minimum peaks found in the difference synthesis were 0.7 and –0.7 e Å^{-3}, respectively. We did not succeed in improving these results, as better quality crystals were not obtained.

Compound 3. In the course of the refinement large thermal parameters indicated disorder in the central propylene bridge and in one of the ethylene bridges. The disorder in the former group was resolved by refining two positions, each with occupancy 0.5, for the central atom C(13). In the ethylene group, however, the possible disorder could not be resolved. After anisotropic refinement, hydrogen atoms, except in the disordered propanediyl group, were included at calculated positions but were not refined. On the Fourier difference map there still remained a ridge of electron density up to 2.1 e Å^{-3}. On closer inspection, three maxima in an approximately linear arrangement could be distinguished, and as the compound had been recrystallized from acetonitrile, one nitrogen and two carbon atoms were tentatively included at these positions and refined isotropically. The results of the refinement are consistent with the above assumption. The full-matrix least-squares refinement included 4879 reflections with $I \geq 3\sigma(I)$ and converged at $R = 0.045$ and $R_w = 0.043$, with maximum shift/esd = 0.05. The maximum and minimum peaks found in the difference synthesis were 0.39 and –0.42 e Å^{-3}.

Compound 4. The fluorine atoms of the PF_6^- groups occupy disordered positions. They were refined anisotropically with an occupancy factor of 0.5. All hydrogen atoms attached to carbon were included at calculated positions with an overall isotropic temperature factor. Assuming a riding model, their positions were adjusted to those of the atoms to which they are bonded. Least-squares refinement which was performed with two blocks containing 326 and 194 parameters, respectively, and included 1804 reflections with $I \geq 2.5\sigma(I)$, converging at $R = 0.059$ and $R_w = 0.063$, with maximum shift/esd = 0.1. The maximum and minimum peaks found in the difference synthesis were 0.4 and –0.4 e Å^{-3}.

Table II. Final Atomic Coordinates (×10^4, Cu × 10^5) of $C_{19}H_{38}Cl_2Cu_3N_6O_{14}$ (**1**)

atom	x/a	y/b	z/c	B_{EQ},[a] Å^2
Cu(1)	17874(6)	–30795(11)	–15045(16)	4.60(6)
Cu(2)	13050(4)	0	14486(13)	3.10(5)
Cu(3)	5074(5)	29652(11)	39384(14)	3.63(5)
O(1)	1656(3)	–2684(5)	730(9)	4.46(34)
O(2)	1568(4)	–1818(6)	–2052(9)	5.14(41)
O(3)	1445(3)	–1348(6)	2038(9)	4.71(36)
O(4)	1118(3)	427(5)	3644(8)	3.62(29)
O(5)	829(3)	2630(5)	1918(8)	3.60(29)
O(6)	757(3)	1706(5)	4715(9)	3.54(28)
N(1)	2094(3)	–4330(7)	–958(13)	4.32(42)
N(2)	1969(4)	–3298(8)	–3803(11)	4.68(46)
N(3)	1401(3)	–422(7)	–703(10)	3.66(37)
N(4)	1206(3)	1307(6)	827(9)	3.26(33)
N(5)	296(3)	4259(6)	3114(11)	3.58(36)
N(6)	143(4)	3286(6)	5974(10)	4.03(39)
C(1)	2452(7)	–4287(12)	358(24)	8.03(96)
C(2)	1719(6)	–5035(14)	–504(30)	9.40(107)
C(3)	2376(8)	–4578(15)	–2421(27)	9.93(116)
C(4)	2194(9)	–4250(10)	–3871(19)	8.28(95)
C(5)	2331(5)	–2610(10)	–4469(18)	5.89(68)
C(6)	1523(6)	–3273(16)	–4891(17)	7.64(89)
C(7)	1534(5)	–1818(8)	814(13)	4.32(53)
C(8)	1484(4)	–1321(8)	–809(11)	3.40(42)
C(9)	1384(5)	159(8)	–2249(13)	4.70(52)
C(10)	1559(5)	1141(9)	–1900(15)	4.88(56)
C(11)	1238(5)	1719(8)	–712(13)	4.44(51)
C(12)	953(3)	1270(7)	3578(12)	3.25(40)
C(13)	1003(3)	1788(7)	2012(12)	3.33(42)
C(14)	–82(5)	4136(10)	1824(15)	5.49(61)
C(15)	725(5)	4784(9)	2467(21)	5.89(64)
C(16)	80(5)	4756(8)	4535(15)	4.84(55)
C(17)	–185(5)	4091(11)	5547(14)	5.56(63)
C(18)	–135(6)	2476(11)	6629(16)	5.59(65)
C(19)	536(6)	3630(12)	7186(19)	6.92(79)
CL(1)	–409(1)	1499(2)	1605(3)	4.20(10)
CL(2)	1937(1)	3340(2)	4528(5)	6.14(16)
O(7)	–285(3)	2052(7)	2993(9)	6.07(41)
O(8)	–435(5)	2084(9)	273(12)	9.59(67)
O(9)	–875(4)	1062(9)	1870(15)	8.84(62)
O(10)	–31(4)	861(11)	1386(18)	11.51(87)
O(11)	1476(3)	3632(10)	5005(18)	10.07(69)
O(12)	1907(5)	2416(8)	3804(15)	9.22(67)
O(13)	2335(13)	3419(32)	5652(36)	10.60(196)
O(13)′	2039(15)	3143(22)	6316(38)	10.57(196)
O(14)	2073(11)	4008(12)	3416(29)	8.28(120)
O(14)′	2357(12)	3641(37)	4583(61)	13.15(257)

[a] $B_{EQ} = 8\pi^2/3\sum U_{ij}A_i^*A_j^*A_i A_j$.

The final positional and thermal parameters of non-hydrogen atoms for the four structures are listed in Tables II–V. Listings of positional and thermal parameters for hydrogen atoms, complete bond lengths and angles, and anisotropic temperature factors are included as supplementary material (Tables S1–S5 for compound **1**, S6–S9 for compound **2**, S10–S14 for compound **3**, and S15–S19 for compound **4**).

Physical Measurements. For the products (**1**–**3**), the magnetic susceptibility of the powdered samples was measured at a 14-kG field on a MANICS-DSM8 susceptometer equipped with an Oxford Instruments liquid-helium cryostat, working down to 4.2 K. For compounds **4** and **5** the magnetic measurements were performed with a Faraday type magnetometer equipped with an Oxford Instruments continuous-flow cryostat working in the 4.2–300 K temperature range. The independence of the susceptibility versus the applied field was checked at room temperature for all compounds. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard.

EPR spectra were recorded on powder samples at the X-band frequency with a Bruker ER200D spectrometer equipped with a cryostat working in the 100–300 K temperature range. The magnetic field was determined with a Hall Probe. DPPH was used as a frequency standard.

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(11) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(12) Frez, B. A. *The SDP-User's Guide* (*SDPVAX, V.3*); Enraf-Nonius: Delft, The Netherlands, 1985.
(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99 (Table 2.2B).

Table III. Final Atomic Coordinates (×10^4) of $C_{35}H_{77}Cl_2Cu_3N_8O_{14}\cdot{}^1/_2H_2O$

atom[a]	*x/a*	*y/b*	*z/c*	B_{EQ},[b] Å^2
Cu(1)A	−33(2)	2468(2)	−3882(3)	5.11(23)
Cu(2)A	1781(2)	1085(2)	−1007(3)	5.32(26)
Cu(3)A	3748(2)	−226(2)	1766(3)	5.38(23)
N(1)A	−825(14)	1666(14)	−4661(26)	6.49(194)
C(2)A	−746(21)	957(25)	−3995(31)	10.62(298)
C(3)A	−1339(28)	332(32)	−4586(42)	15.41(443)
C(4)A	−805(33)	1615(39)	−5574(36)	14.88(477)
C(5)A	−169(33)	1157(27)	−5549(36)	13.14(402)
C(6)A	−1541(21)	2083(42)	−4795(40)	15.72(441)
C(7)A	−1496(27)	2902(28)	−4972(42)	12.80(371)
N(8)A	−816(15)	3237(15)	−4160(30)	7.54(208)
C(9)A	−924(17)	3575(26)	−3332(29)	8.51(285)
C(10)A	−1378(28)	4236(32)	−3567(31)	14.77(411)
C(11)A	−535(27)	3871(23)	−4718(29)	9.33(297)
C(12)A	252(27)	4059(23)	−4175(29)	9.35(292)
N(13)A	673(17)	3397(15)	−3950(27)	7.86(226)
C(14)A	770(17)	3117(16)	−4878(28)	6.38(218)
C(15)A	1253(19)	3702(25)	−5215(29)	11.57(301)
C(16)A	1408(20)	3567(23)	−3023(38)	9.82(300)
C(17)A	1267(21)	3803(29)	−2187(30)	10.85(342)
O(18)A	60(9)	2181(11)	−2395(12)	4.65(113)
O(19)A	772(9)	1803(11)	−3569(18)	5.03(129)
C(20)A	602(18)	1762(16)	−2045(32)	4.42(223)
C(21)A	1049(24)	1601(20)	−2699(30)	5.90(264)
O(22)A	840(10)	1550(12)	−1228(18)	5.29(136)
N(23)A	1651(15)	1198(15)	−2325(17)	5.18(167)
C(24)A	2083(18)	1048(17)	−2837(27)	6.36(238)
C(25)A	2538(22)	382(23)	−2360(28)	9.04(294)
C(26)A	3086(17)	508(24)	−1419(27)	7.97(268)
N(27)A	2663(14)	599(15)	−803(27)	4.79(188)
O(28)A	1834(11)	746(13)	257(13)	5.87(135)
C(29)A	3018(35)	381(17)	89(43)	6.83(404)
C(30)A	2494(25)	487(21)	628(32)	8.22(274)
O(31)A	3583(10)	113(15)	518(17)	7.19(147)
O(32)A	2650(9)	188(11)	1420(17)	4.80(123)
N(33)A	3960(16)	−1295(17)	1256(29)	8.08(229)
C(34)A	3378(21)	−1736(20)	479(24)	8.78(232)
C(35)A	2639(23)	−1664(30)	613(33)	12.98(353)
C(36)A	4639(22)	−1159(32)	1141(45)	15.43(438)
C(37)A	4799(39)	−1909(33)	617(36)	18.57(537)
C(38)A	4113(21)	−1681(31)	2063(47)	9.94(364)
C(39)A	4244(31)	−1453(30)	2955(40)	15.01(452)
N(40)A	3800(41)	−758(23)	3048(25)	19.06(398)
C(41)A	3079(29)	−915(38)	3146(47)	14.68(498)
C(42)A	3208(31)	−1240(29)	4077(31)	15.74(440)
C(43)A	4251(39)	−259(42)	3571(58)	15.78(605)
C(44)A	4691(35)	418(32)	3489(32)	17.51(413)
N(45)A	4389(20)	728(14)	2574(23)	8.90(219)
C(46)A	3760(26)	1327(25)	2471(28)	11.31(313)
C(47)A	4091(31)	2054(29)	3213(41)	15.86(450)
C(48)A	4925(32)	1207(30)	1847(35)	15.19(400)
C(49)A	5153(72)	785(53)	1351(88)	38.41(810)
CU(1)B	10303(2)	2559(3)	1352(3)	6.86(29)
CU(2)B	8441(2)	4065(2)	2347(3)	4.96(24)
CU(3)B	6277(2)	5096(2)	3122(3)	5.29(24)
N(1)B	10950(14)	3396(15)	999(28)	6.85(204)
C(2)B	10902(20)	4212(20)	1439(31)	9.62(290)
C(3)B	11374(23)	4889(25)	1289(33)	11.47(322)
C(4)B	10820(22)	3326(21)	−51(32)	7.37(280)
C(5)B	10126(25)	3732(22)	−529(28)	9.71(300)
C(6)B	11704(21)	3155(23)	1515(28)	8.72(277)
C(7)B	11714(17)	2250(22)	1508(29)	7.56(262)
N(8)B	11202(20)	1937(22)	1937(30)	8.75(272)
C(9)B	11524(25)	2103(33)	2937(39)	13.49(403)
C(10)B	2121(20)	1670(33)	−6695(40)	17.33(426)
C(11)B	11029(26)	1143(29)	1672(33)	9.90(327)
C(12)B	10356(23)	1009(23)	649(32)	9.33(295)
N(13)B	9803(20)	1592(23)	673(30)	10.54(287)
C(14)B	−647(23)	1837(30)	−10445(35)	10.39(340)
C(15)B	−948(34)	1231(35)	−11065(70)	22.14(615)
C(16)B	−701(44)	1370(35)	1076(86)	27.81(681)
C(17)B	−747(44)	713(48)	1590(49)	21.69(726)
O(18)B	10184(11)	2982(12)	2624(13)	5.57(128)
O(19)B	9403(12)	3071(14)	765(19)	6.80(172)
C(20)B	9608(18)	3368(18)	2404(33)	4.87(255)
C(21)B	9195(24)	3392(27)	1348(32)	6.77(310)
O(22)B	9437(11)	3706(12)	3051(16)	6.07(142)
N(23)B	8563(15)	3782(12)	1205(19)	3.56(156)
C(24)B	8104(15)	3811(18)	228(22)	5.51(189)
C(25)B	7628(20)	4481(27)	113(24)	10.62(300)
C(26)B	7063(18)	4433(22)	652(26)	6.84(239)
N(27)B	7507(12)	4462(12)	1669(26)	4.14(166)
O(28)B	8299(11)	4440(11)	3492(13)	4.76(123)
C(29)B	7185(19)	4653(13)	2207(25)	3.11(188)
C(30)B	7651(18)	4689(15)	3262(28)	3.24(209)
O(31)B	6522(10)	4840(10)	2049(14)	5.15(119)
O(32)B	7420(9)	4942(10)	3890(16)	3.92(120)
N(33)B	5871(19)	3937(16)	3296(25)	7.29(216)
C(34)B	5232(22)	3622(29)	2497(39)	11.36(328)
C(35)B	5565(25)	3282(27)	1817(38)	12.03(366)
C(36)B	6544(20)	3505(19)	3751(27)	7.94(243)
C(37)B	6301(30)	2646(22)	4025(30)	13.26(353)
C(38)B	5471(29)	4060(32)	3961(44)	12.79(422)
C(39)B	5869(23)	4718(34)	4632(32)	9.76(346)
N(40)B	6150(19)	5469(17)	4301(22)	6.07(203)
C(41)B	6713(28)	5947(34)	4878(38)	12.00(402)
C(42)B	−3471(28)	6277(30)	−4221(32)	14.63(412)
C(43)B	5465(21)	5959(27)	3877(32)	10.15(309)
C(44)B	5476(20)	6459(19)	3076(35)	7.82(277)
N(45)B	5707(16)	6021(15)	2431(24)	7.00(188)
C(46)B	5024(25)	5734(32)	1599(48)	15.22(389)
C(47)B	5471(25)	3951(30)	−916(32)	16.34(376)
C(48)B	6193(32)	6580(27)	2092(37)	12.59(411)
C(49)B	6872(20)	6794(29)	2659(27)	10.00(291)
CL(1)A	3011(7)	2822(7)	21(12)	2.05(77)
CL(2)A	6777(12)	3625(10)	7017(14)	5.59(109)
CL(1)B	7580(6)	2209(6)	2202(9)	1.52(60)
CL(2)B	3559(9)	1271(14)	5741(13)	4.44(106)
*O(1)A	2441(21)	2474(21)	−329(24)	5.30(30)
*O(2)A	3547(23)	2580(23)	−91(28)	7.73(36)
*O(3)A	3086(27)	2774(30)	669(42)	9.82(67)
*O(4)A	2955(24)	3513(32)	65(33)	9.78(43)
*O(5)A	6170(20)	3299(21)	6526(26)	5.35(29)
*O(6)A	7025(31)	4363(39)	7112(40)	14.19(59)
*O(7)A	7055(40)	3318(46)	7253(57)	12.41(108)
*O(8)A	6665(41)	3643(47)	635(62)	15.10(105)
*O(1)B	7917(15)	2762(18)	2727(22)	3.37(23)
*O(2)B	7048(22)	2520(24)	1500(30)	8.02(37)
*O(3)B	7390(25)	1857(29)	2667(36)	9.08(48)
*O(4)B	−2051(27)	1866(30)	−8056(36)	10.59(49)
*O(5)B	3826(23)	1214(24)	6630(39)	8.71(41)
*O(6)B	3063(31)	1636(32)	5731(36)	11.75(50)
*O(7)B	3334(40)	857(44)	5545(54)	9.35(120)
*O(8)B	3879(37)	1652(39)	5512(48)	13.56(73)
*Ow	3687(22)	4432(24)	2208(29)	8.48(38)

[a] An asterisk indicates an isotropically refined atom. [b] $B_{EQ} = 8\pi^2/3\sum U_{ij}A_i^*A_j^*A_i\cdot A_j$.

Results

Description of Structures. [{(tmen)Cu}$_2${μ-Cu(pba)}](ClO$_4$)$_2$ (1). The trinuclear cation of compound **1** is shown in Figure 1. Bond lengths and angles in the copper coordination sphere are listed in Table VI. The terminal copper ions Cu(1) and Cu(3) have 4 + 1 and a 4 + 2 coordination, respectively, their basal planes being formed by two nitrogen atoms from the tmen ligand and two oxygen atoms from the oxamato bridge. The square-pyramidal coordination sphere of Cu(1) is completed by an apical oxygen atom O(9) from one perchlorate anion at 2.723 Å. The metal atom is displaced from the least-squares basal plane toward the apical oxygen by 0.108 Å. The axial positions of Cu(3) are occupied by the oxygen atoms O(7) and O(11) from perchlorate anions at 2.587 and 2.875 Å, leading to a Jahn–Teller distorted octahedral coordination. The copper atom does not deviate significantly from the mean plane. The central Cu(2) atom is quasi square-planar, with a weak tetrahedral distortion evaluated through the Galy[14] parameter as 9%. We attribute this distortion to the second-order Jahn–Teller effect on the copper(II) square-planar ion.[15] The Cu···Cu separations within the trinuclear unit

Table IV. Final Atomic Coordinates (×10^4, Cu × 10^5) of $C_{73}H_{92}B_2Cu_3N_8O_6 \cdot CH_3CN$(3). * atoms are refined isotropically.

atom[a]	x/a	y/b	z/c	B_{EQ},[b] Å^2	atom[a]	x/a	y/b	z/c	B_{EQ},[b] Å^2
Cu(1)	71524(7)	7389(2)	73679(5)	3.50(2)	C(113)	9650(6)	2878(2)	4660(4)	5.6(2)
Cu(2)	44439(7)	13605(2)	51265(5)	4.07(2)	C(114)	9961(6)	3198(2)	4301(4)	6.9(2)
Cu(3)	17780(7)	19188(2)	28083(5)	3.88(2)	C(115)	9259(7)	3353(2)	3723(5)	8.3(3)
O(1)	6396(3)	1287(1)	7096(2)	4.4(1)	C(116)	8207(7)	3193(2)	3510(5)	7.2(3)
O(2)	6321(3)	607(1)	6362(2)	3.8(1)	C(121)	6629(5)	2235(2)	3770(4)	3.6(2)
O(3)	5183(4)	1519(1)	6156(2)	4.3(1)	C(122)	6612(5)	1969(2)	3166(4)	4.4(2)
O(4)	3672(4)	1833(1)	4923(2)	4.5(1)	C(123)	6693(6)	1582(2)	3302(5)	5.8(2)
O(5)	2432(4)	1434(1)	3171(2)	4.5(1)	C(124)	6826(6)	1447(2)	4059(5)	6.5(2)
O(6)	2541(4)	2096(1)	3961(2)	4.5(1)	C(125)	6829(6)	1692(2)	4669(5)	6.4(2)
N(1)	8638(4)	742(2)	6907(3)	4.7(2)	C(126)	6723(6)	2075(2)	4523(4)	5.0(2)
N(2)	8016(4)	854(2)	8398(3)	4.6(2)	C(131)	6134(6)	2805(2)	2746(4)	4.3(2)
N(3)	6056(4)	472(2)	8006(3)	4.5(2)	C(132)	6751(6)	2730(2)	2106(4)	6.3(2)
N(4)	5125(4)	877(1)	5374(3)	3.9(1)	C(133)	6345(8)	2808(3)	1335(4)	8.7(3)
N(5)	3712(4)	1192(1)	4136(3)	4.3(1)	C(134)	5307(8)	2962(2)	1165(5)	8.6(3)
N(6)	192(4)	1790(2)	3022(3)	4.4(2)	C(135)	4696(7)	3045(2)	1755(5)	7.1(2)
N(7)	1157(4)	2409(2)	2398(3)	4.6(2)	C(136)	5102(6)	2964(2)	2523(4)	5.2(2)
N(8)	2857(4)	1959(2)	1961(3)	4.6(2)	C(141)	5780(5)	2890(2)	4249(4)	4.0(2)
*N(9)	6427(7)	3878(3)	283(5)	12.7(3)	C(142)	5946(6)	3255(2)	4568(4)	4.6(2)
C(1)	8915(7)	348(2)	6745(5)	8.0(3)	C(143)	5235(6)	3420(2)	5041(4)	5.8(2)
C(2)	8647(6)	962(2)	6155(5)	7.3(3)	C(144)	4294(6)	3235(2)	5216(4)	6.4(2)
C(3)	9452(6)	909(2)	7505(5)	6.5(2)	C(145)	4088(6)	2877(2)	4918(4)	5.9(2)
C(4)	9194(6)	774(2)	8304(4)	6.3(2)	C(146)	4823(6)	2711(2)	4445(4)	5.0(2)
C(5)	7880(6)	1252(2)	8592(5)	7.5(2)	C(211)	7053(5)	5213(2)	2216(4)	3.7(2)
C(6)	7582(6)	599(2)	8999(4)	6.8(2)	C(212)	6845(6)	5506(2)	1691(4)	5.6(2)
C(7)	6331(6)	586(2)	8825(4)	6.8(2)	C(213)	6798(8)	5459(2)	889(4)	8.5(3)
C(8)	4879(6)	573(2)	7767(5)	6.8(2)	C(214)	7032(8)	5116(3)	581(4)	9.5(3)
C(9)	6197(7)	65(2)	7894(5)	7.4(3)	C(215)	7280(8)	4822(2)	1073(5)	8.7(3)
C(10)	5784(5)	1255(2)	6477(4)	3.8(2)	C(216)	7291(6)	4874(2)	1878(4)	5.4(2)
C(11)	5755(5)	881(2)	6042(3)	2.9(2)	C(221)	7472(5)	4927(2)	3697(4)	3.3(2)
C(12)	5041(6)	519(2)	4914(4)	4.7(2)	C(222)	6983(5)	4570(2)	3591(4)	4.3(2)
*C(13)Y	3970(10)	527(4)	4345(7)	4.1(3)	C(223)	7338(6)	4255(2)	4014(4)	5.4(2)
*C(13)X	4750(10)	598(4)	4039(8)	4.3(3)	C(224)	8217(6)	4281(2)	4594(4)	5.7(2)
C(14)	3762(7)	818(2)	3762(4)	6.1(2)	C(225)	8689(6)	4625(2)	4751(4)	4.7(2)
C(15)	3086(5)	1825(2)	4265(4)	3.7(2)	C(226)	8340(5)	4940(2)	4299(4)	3.7(2)
C(16)	3074(5)	1450(2)	3821(3)	3.7(2)	C(231)	7799(5)	5654(2)	3402(3)	3.2(2)
C(17)	−210(7)	1467(3)	2555(6)	9.6(3)	C(232)	7519(5)	5954(2)	3860(4)	4.1(2)
C(18)	66(7)	1711(4)	3838(5)	13.5(4)	C(233)	8263(6)	6238(2)	4102(4)	5.3(2)
C(19)	−428(7)	2109(3)	2771(8)	14.7(4)	C(234)	9318(6)	6229(2)	3888(4)	5.2(2)
C(20)	−56(6)	2393(2)	2411(5)	8.4(3)	C(235)	9627(5)	5944(2)	3415(4)	5.2(2)
C(21)	1615(7)	2730(2)	2863(5)	7.1(3)	C(236)	8880(6)	5665(2)	3173(4)	4.7(2)
C(22)	1441(6)	2431(2)	1593(5)	7.1(2)	C(241)	5731(5)	5366(2)	3361(4)	3.3(2)
C(23)	2590(7)	2315(2)	1548(5)	7.4(3)	C(242)	4877(5)	5483(2)	2812(4)	4.6(2)
C(24)	2646(6)	1628(2)	1432(4)	6.5(2)	C(243)	3835(6)	5581(2)	3011(4)	5.9(2)
C(25)	4039(6)	1958(2)	2277(5)	7.0(2)	C(244)	3586(5)	5551(2)	3772(5)	5.5(2)
*C(27)	6920(8)	3802(3)	895(6)	10.9(3)	C(245)	4404(6)	5430(2)	4338(4)	5.4(2)
*C(28)	7430(8)	3716(3)	1651(6)	10.0(3)	C(246)	5445(5)	5338(2)	4127(4)	4.6(2)
C(111)	7863(5)	2866(2)	3860(4)	3.9(2)	B(1)	6601(7)	2694(2)	3661(5)	3.8(2)
C(112)	8618(6)	2719(2)	4439(4)	4.5(2)	B(2)	7018(6)	5288(2)	3161(4)	3.3(2)

[a] An asterisk indicates an isotropically refined atom. [b] $B_{EQ} = 8\pi^2/3\sum U_{ij}A_i^*A_j^*A_i \cdot A_j$.

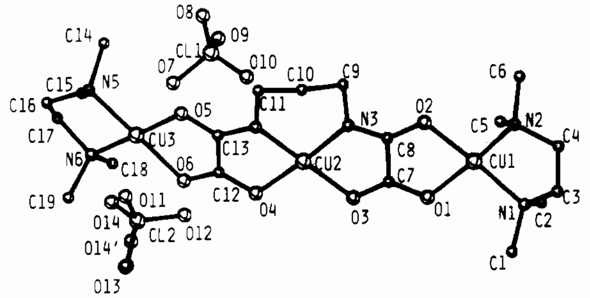

Figure 1. Plot of the trinuclear cation of $\{[Cu(tmen)]_2[\mu\text{-}Cu(pba)]\}(ClO_4)_2$ (1), showing the atom-numbering scheme.

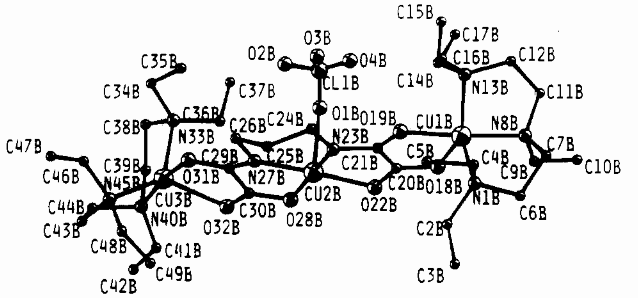

Figure 2. Plot of the trinuclear cation of $\{[Cu(pet)]_2(\mu\text{-}Cu(pba)]\}(ClO_4)_2 \cdot {}^1/_2H_2O$ (2), showing the atom-numbering scheme.

are Cu(1)–Cu(2) = 5.146 Å and Cu(2)–Cu(3) = 5.119 Å. The shortest Cu–Cu intermolecular distances are 5.986, 6.583, and 6.789 Å for Cu(1)–Cu(2)′ ($^1/_2 + x$, $y - ^1/_2$, $z - ^1/_2$), Cu(1)–Cu(3)″ ($-x$, $y - ^1/_2$, $-z$), and Cu(2)–Cu(3)‴ ($-x$, $y - ^1/_2$, $1 - z$), respectively.

$[\{(pet)Cu\}_2\{\mu\text{-}Cu(pba)\}](ClO_4)_2 \cdot {}^1/_2H_2O$ (2). The structure of complex **2** is made up of two different, but closely similar, cationic copper(II) trinuclear units A and B. The former is depicted in Figure 2 with its labeling scheme. The main bond lengths and angles are given for the A and B units in Table VII.

The central copper atoms have approximately square-pyramidal coordination. In the basal plane they are surrounded by two nitrogen atoms and two oxygen atoms of the oxamato bridges. The apical positions are occupied by oxygen atoms of perchlorate ions at 2.73 and 2.64 Å for Cu(2)A–O(1)A and Cu(2)B–O(1)B, respectively. The copper atoms are displaced from the mean

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(14) Galy, J.; Bonnet, J. J.; Anderson, S. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 383.

(15) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, *A161*, 220.

Table V. Final Atomic Coordinates (×10^4) of $C_{19}H_{42}Cu_3F_{12}N_8O_7P_2$ (4)

atom	x/a	y/b	z/c	B_{EQ},[a] Å^2	atom	x/a	y/b	z/c	B_{EQ},[a] Å^2
Cu(1)	2565(1)	1378(2)	3850(2)	3.92(12)	C(26)	502(5)	−222(11)	−3714(15)	4.78(106)
Cu(2)	1399(1)	1321(1)	1368(2)	3.26(10)	N(27)	544(4)	−907(8)	−2871(11)	3.61(73)
Cu(3)	561(1)	−489(1)	−1138(2)	3.11(10)	C(28)	858(5)	−1361(13)	−3207(17)	4.83(112)
N(1)	2613(4)	186(10)	4162(16)	5.73(101)	C(29)	887(5)	−2122(14)	−2437(21)	6.52(141)
C(1)	2775(6)	−290(15)	3202(22)	8.20(170)	C(30)	1035(5)	−1922(12)	−1188(18)	5.41(117)
C(2)	3124(6)	82(18)	2894(28)	9.03(207)	N(31)	793(4)	−1486(9)	−479(14)	5.15(90)
C(3)	3130(8)	820(20)	2385(22)	8.43(189)	Ow	1178(4)	2657(8)	1107(11)	7.36(84)
N(4)	3052(4)	1457(11)	3281(13)	4.06(84)	P(1)	1728(2)	3888(4)	3469(7)	6.54(41)
C(4)	3139(6)	2250(19)	2799(21)	8.34(183)	P(2)	146(2)	2353(4)	388(6)	5.47(33)
C(5)	3101(6)	2861(16)	3757(32)	10.98(214)	F(1)	1840(13)	3418(23)	4695(45)	7.83(231)
C(6)	2755(5)	3104(15)	4084(24)	8.87(178)	F(1)′	1961(13)	3713(35)	4508(50)	14.47(401)
N(7)	2551(4)	2473(9)	4577(14)	4.25(82)	F(2)	1429(4)	3290(11)	3511(16)	14.05(132)
O(8)	2377(3)	1580(8)	2010(9)	4.41(69)	F(3)	1970(9)	−339(16)	1508(37)	7.64(187)
C(9)	2062(4)	1523(10)	1975(15)	2.71(90)	F(3)′	2072(13)	4247(22)	3527(67)	14.94(360)
O(10)	1879(3)	1585(8)	1041(9)	4.16(65)	F(4)	1932(15)	3435(31)	2413(45)	15.93(356)
O(11)	2053(3)	1247(7)	4118(10)	3.78(64)	F(4)′	1935(8)	3271(25)	2755(34)	5.45(23)
C(12)	1879(4)	1339(10)	3150(15)	2.43(83)	F(5)	1499(9)	4409(26)	4355(38)	6.82(156)
N(13)	1556(3)	1292(8)	3024(11)	3.11(73)	F(5)′	1539(22)	4392(60)	4121(79)	19.87(119)
C(14)	1327(5)	1062(12)	4070(14)	4.63(106)	F(6)	1532(7)	4218(17)	2381(22)	6.62(143)
C(15)	939(5)	1219(11)	3731(14)	4.44(102)	F(6)′	1712(17)	4313(46)	2185(68)	22.01(98)
C(16)	812(5)	627(12)	2751(16)	4.60(111)	F(7)	−138(14)	2863(23)	1052(71)	8.31(235)
N(17)	966(3)	802(9)	1606(11)	3.23(74)	F(7)′	215(14)	−2583(22)	−1044(73)	6.39(221)
C(18)	853(4)	492(12)	643(17)	3.81(103)	F(8)	289(16)	2165(53)	1513(36)	27.96(613)
O(19)	606(3)	−15(6)	539(9)	3.26(61)	F(8)′	−392(8)	−2792(20)	−1230(32)	6.12(180)
O(20)	1305(3)	1142(7)	−363(9)	3.26(61)	F(9)	101(7)	1526(11)	1073(25)	5.32(145)
C(21)	1060(4)	671(11)	−514(17)	3.14(96)	F(10)	473(3)	2000(6)	−244(12)	8.06(74)
O(22)	979(3)	359(7)	−1476(10)	3.93(65)	F(11)	−104(4)	1924(10)	−455(15)	12.89(118)
N(23)	151(3)	244(9)	−1351(11)	3.63(72)	F(12)	143(9)	2939(19)	−628(27)	7.19(186)
C(24)	153(5)	731(10)	−2461(15)	4.12(100)	F(12)′	−239(15)	−3209(19)	−76(81)	21.12(492)
C(25)	172(5)	210(12)	−3605(17)	4.79(108)					

[a] $B_{EQ} = 8\pi^2/3\sum U_{ij}A_i{}^*A_j{}^*A_i{\cdot}A_j$.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $C_{19}H_{38}Cl_2Cu_3N_6O_{14}$ (1)

O(1)–Cu(1)	1.973(8)	N(4)–Cu(2)	1.930(8)
O(2)–Cu(1)	1.923(8)	O(5)–Cu(3)	1.945(7)
N(1)–Cu(1)	1.992(10)	O(6)–Cu(3)	1.999(7)
N(2)–Cu(1)	1.998(10)	N(5)–Cu(3)	2.025(9)
O(3)–Cu(2)	1.995(8)	N(6)–Cu(3)	2.004(9)
O(4)–Cu(2)	1.988(7)	O(7)–Cu(3)	2.587(9)
N(3)–Cu(2)	1.905(8)		

O(2)–Cu(1)–O(1)	84.8(3)	N(4)–Cu(2)–N(3)	93.6(4)
N(1)–Cu(1)–O(1)	96.1(4)	O(6)–Cu(3)–O(5)	85.4(3)
N(1)–Cu(1)–O(2)	173.5(4)	N(5)–Cu(3)–O(5)	92.6(3)
N(2)–Cu(1)–O(1)	171.7(4)	N(5)–Cu(3)–O(6)	176.7(3)
N(2)–Cu(1)–O(2)	89.3(4)	N(6)–Cu(3)–O(5)	177.1(3)
N(2)–Cu(1)–N(1)	89.1(4)	N(6)–Cu(3)–O(6)	94.9(3)
O(4)–Cu(2)–O(3)	96.2(3)	N(6)–Cu(3)–N(5)	87.2(4)
N(3)–Cu(2)–O(3)	84.8(3)	O(7)–Cu(3)–O(5)	88.4(3)
N(3)–Cu(2)–O(4)	173.3(3)	O(7)–Cu(3)–O(6)	85.8(3)
N(4)–Cu(2)–O(3)	176.9(4)	O(7)–Cu(3)–N(5)	96.8(3)
N(4)–Cu(2)–O(4)	85.6(3)	O(7)–Cu(3)–N(6)	88.7(3)

basal planes toward the apical sites by 0.12 Å for the A unit and by 0.06 Å for B. A weak tetrahedral distortion is observed in Cu(2)A and evaluated through the Galy[14] formula as 9.6%. All terminal copper atoms are in similar environments, intermediate between tbp and square-planar coordinations, although the former character is clearly dominant, as expected for the bulky ethyl N-substituents. Deviations from these ideal geometries will be analyzed later for all products.

The Cu–Cu separations within each trinuclear unit are Cu(1A)–Cu(2A) = 5.284 Å, Cu(2A)–Cu(3A) = 5.269 Å and Cu(1B)–Cu(2B) = 5.259 Å, Cu(2B)–Cu(3B) = 5.246 Å. The shortest Cu–Cu intermolecular distances are 6.017, 6.245, and 6.734 Å for Cu(2A)–Cu(1B)′ ($x-1, y, z$), Cu(1A)–Cu(2B)″ ($x-1, y, z-1$), and Cu(1A)–Cu(2B)‴ ($1-x, 1-y, -z$), respectively.

[{(pmd)Cu}$_2${μ-Cu(pba)}](BPh$_4$)$_2$·CH$_3$CN (3). Compound **3** forms trinuclear cations well separated from the anions. The trinuclear {[Cu(pmd)]$_2$[μ-Cu(pba)]}$^{2+}$ cation with the atom numbering used is shown in Figure 3. Selected bond distances and angles are presented in Table VIII.

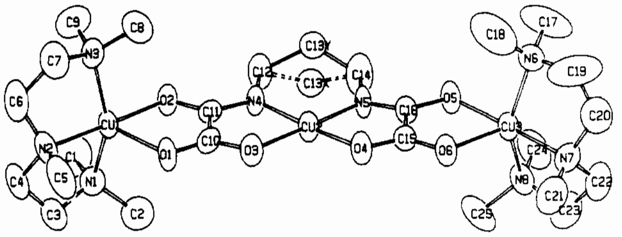

Figure 3. Plot of the trinuclear cation of {[Cu(pmd)]$_2$[μ-Cu(pba)]}(BPh$_4$)$_2$·CH$_3$CN (3), showing the atom-numbering scheme.

The central copper atom, Cu(2), has approximately square-planar coordination with a slight tetrahedral distortion. The copper atom is displaced 0.045 Å from a least-squares plane defined by the ligand atoms. The two terminal copper atoms have similar coordination, intermediate between square-pyramidal and trigonal-bipyramidal. Considering a distorted sqp geometry, the equatorial ligand atoms of Cu(1) (N(1), N(2), N(3), O(2)) deviate by 0.23–0.26 Å from an optimal least-squares plane, and the copper atom is displaced 0.28 Å from this plane toward the axial ligand, the oxamato oxygen O(1). An equivalent description of Cu(3) shows deviations in the range 0.27–0.31 Å for the equatorial ligand atoms (N(6), N(7), N(8), O(5)) and a displacement of 0.31 Å for copper toward axial oxamato oxygen O(6). The dihedral angles between the equatorial plane of the central copper atom and the two terminal copper atoms are 86.2 and 93.6°, respectively. If a tbp description is considered, the axial ligands for Cu(1) are O(2) and N(2) and for Cu(3) are N(7) and O(5).

The intramolecular Cu---Cu distances across oxamato bridges are Cu(1)---Cu(2) = 5.276(1) Å and Cu(2)---Cu(3) = 5.249(1) Å. The shortest intermolecular metal–metal distance occurs between molecules related by an n-glide translation, Cu(2)---Cu(3) ($^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$) = 7.980(1) Å.

[{(bapa)Cu}$_2${μ-Cu(pba)(H$_2$O)}](PF$_6$)$_2$ (4). Compound **4** crystallizes as an ionic structure where the [{(bapa)Cu}$_2${μ-Cu(pba)(H$_2$O)}]$^{2+}$ cations are well separated from the PF$_6$$^-$ anions. Its

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $C_{35}H_{77}Cl_2Cu_3N_8O_{14}\cdot{}^1/_2H_2O$ (**2**)

	molecule A	molecule B		molecule A	molecule B
N(1)–Cu(1)	2.09(2)	2.13(3)	O(28)–Cu(2)	2.00(2)	1.98(2)
N(8)–Cu(1)	2.03(3)	2.06(4)	O(1)–Cu(2)	2.73(3)	2.64(3)
N(13)–Cu(1)	2.15(3)	2.01(4)	O(31)–Cu(3)	1.93(3)	1.93(3)
O(18)–Cu(1)	2.29(2)	2.16(2)	O(32)–Cu(3)	2.22(2)	2.20(2)
O(19)–Cu(1)	1.94(2)	1.95(2)	N(33)–Cu(3)	2.12(3)	2.21(2)
O(22)–Cu(2)	1.99(2)	2.03(2)	N(40)–Cu(3)	2.16(4)	2.01(4)
N(23)–Cu(2)	1.96(3)	1.91(3)	N(45)–Cu(3)	2.15(3)	2.08(3)
N(27)–Cu(2)	1.91(3)	1.94(2)			

	molecule A	molecule B		molecule A	molecule B
N(8)–Cu(1)–N(1)	86.8(11)	88.1(14)	O(28)–Cu(2)–N(27)	88.2(14)	86.2(13)
N(13)–Cu(1)–N(1)	145.1(15)	130.8(18)	O(1)–Cu(2)–O(22)	89.3(9)	89.0(9)
N(13)–Cu(1)–N(8)	87.7(12)	88.1(15)	O(1)–Cu(2)–N(23)	98.8(10)	100.7(10)
O(18)–Cu(1)–N(1)	101.1(12)	106.4(12)	O(1)–Cu(2)–N(27)	92.9(10)	93.9(10)
O(18)–Cu(1)–N(8)	98.9(14)	98.7(14)	O(1)–Cu(2)–O(28)	93.0(10)	83.1(10)
O(18)–Cu(1)–N(13)	113.8(11)	122.6(16)	O(32)–Cu(3)–O(31)	80.9(9)	83.4(9)
O(19)–Cu(1)–N(1)	98.0(9)	95.7(11)	N(33)–Cu(3)–O(31)	84.8(14)	96.8(12)
O(19)–Cu(1)–N(8)	175.3(9)	175.3(13)	N(33)–Cu(3)–O(32)	122.5(9)	98.5(10)
O(19)–Cu(1)–N(13)	88.1(10)	87.3(13)	N(40)–Cu(3)–O(31)	170.3(15)	171.4(11)
O(19)–Cu(1)–O(18)	80.7(10)	82.8(10)	N(40)–Cu(3)–O(32)	95.6(22)	90.6(12)
N(23)–Cu(2)–O(22)	90.2(12)	88.8(11)	N(40)–Cu(3)–N(33)	89.5(17)	90.1(14)
N(27)–Cu(2)–O(22)	177.7(10)	177.1(9)	N(45)–Cu(3)–O(31)	100.4(12)	90.3(12)
N(27)–Cu(2)–N(23)	90.0(15)	91.2(14)	N(45)–Cu(3)–O(32)	102.1(11)	132.8(10)
O(28)–Cu(2)–O(22)	91.2(10)	93.7(9)	N(45)–Cu(3)–N(33)	135.3(13)	128.7(12)
O(28)–Cu(2)–N(23)	168.1(10)	175.5(9)	N(45)–Cu(3)–N(40)	89.2(15)	89.3(13)

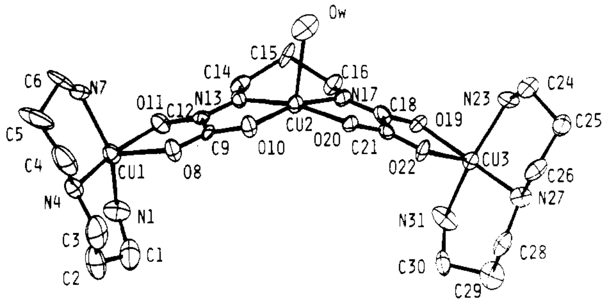

Figure 4. Plot of the trinuclear cation of {[Cu(bapa)]$_2$[μ-Cu(pba)(H$_2$O)]}-(PF$_6$)$_2$ (**4**), showing the atom-numbering scheme.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $C_{73}H_{92}B_2Cu_3N_8O_6\cdot CH_3CN$ (**3**)

O(1)–Cu(1)	2.180(4)	N(5)–Cu(2)	1.927(5)
O(2)–Cu(1)	1.963(4)	O(4)–Cu(2)	1.934(4)
N(1)–Cu(1)	2.037(5)	O(6)–Cu(3)	2.185(4)
N(2)–Cu(1)	2.001(5)	O(5)–Cu(3)	1.968(4)
N(3)–Cu(1)	2.037(5)	N(6)–Cu(3)	2.046(5)
O(3)–Cu(2)	1.976(4)	N(7)–Cu(3)	1.994(5)
N(4)–Cu(2)	1.930(5)	N(8)–Cu(3)	2.053(5)

N(1)–Cu(1)–N(2)	86.2(2)	O(4)–Cu(2)–N(4)	86.4(2)
N(1)–Cu(1)–N(3)	149.3(2)	O(4)–Cu(2)–N(5)	175.7(2)
N(2)–Cu(1)–N(3)	86.3(2)	N(4)–Cu(2)–N(5)	93.9(2)
O(1)–Cu(1)–O(2)	81.8(2)	O(6)–Cu(3)–O(5)	81.1(2)
O(1)–Cu(1)–N(1)	106.4(2)	O(6)–Cu(3)–N(6)	102.9(2)
O(1)–Cu(1)–N(2)	100.2(2)	O(6)–Cu(3)–N(7)	100.3(2)
O(1)–Cu(1)–N(3)	104.2(2)	O(6)–Cu(3)–N(8)	112.0(2)
O(2)–Cu(1)–N(1)	93.4(2)	O(5)–Cu(3)–N(6)	96.0(2)
O(2)–Cu(1)–N(2)	178.0(2)	O(5)–Cu(3)–N(7)	177.4(2)
O(2)–Cu(1)–N(3)	93.1(2)	O(5)–Cu(3)–N(8)	91.1(2)
O(3)–Cu(2)–O(4)	97.4(2)	N(6)–Cu(3)–N(7)	85.9(2)
O(3)–Cu(2)–N(4)	84.9(2)	N(6)–Cu(3)–N(8)	145.0(2)
O(3)–Cu(2)–N(5)	178.4(2)	N(7)–Cu(3)–N(8)	86.3(2)

Table IX. Selected Bond Lengths (Å) and Angles (deg) for $C_{19}H_{42}Cu_3F_{12}N_8O_7P_2$ (**4**)

N(1)–Cu(1)	2.057(16)	O(20)–Cu(2)	1.985(10)
N(4)–Cu(1)	1.998(14)	Ow–Cu(2)	2.438(14)
N(7)–Cu(1)	2.025(15)	O(19)–Cu(3)	2.041(11)
O(8)–Cu(1)	2.203(11)	O(22)–Cu(3)	2.200(12)
O(11)–Cu(1)	2.024(11)	N(23)–Cu(3)	2.031(14)
O(10)–Cu(2)	1.951(11)	N(27)–Cu(3)	2.057(13)
N(13)–Cu(2)	1.943(13)	N(31)–Cu(3)	2.050(15)
N(17)–Cu(2)	1.916(13)		

N(4)–Cu(1)–N(1)	92.0(7)	O(20)–Cu(2)–N(17)	84.4(5)
N(7)–Cu(1)–N(1)	146.5(7)	Ow–Cu2–O(10)	95.8(5)
N(7)–Cu(1)–N(4)	95.2(6)	Ow–Cu(2)–N(13)	104.3(5)
O(8)–Cu(1)–N(1)	109.8(6)	Ow–Cu(2)–N(17)	97.7(5)
O(8)–Cu(1)–N(4)	90.5(5)	Ow–Cu(2)–O(20)	87.7(4)
O(8)–Cu(1)–N(7)	102.7(6)	O(22)–Cu(3)–O(19)	80.6(4)
O(11)–Cu(1)–N(1)	87.4(6)	N(23)–Cu(3)–O(19)	86.2(5)
O(11)–Cu(1)–N(4)	169.7(5)	N(23)–Cu(3)–O(22)	99.1(5)
O(11)–Cu(1)–N(7)	90.8(5)	N(27)–Cu(3)–O(19)	175.6(5)
O(11)–Cu(1)–O(8)	80.1(4)	N(27)–Cu(3)–O(22)	95.0(5)
N(13)–Cu(2)–O(10)	83.3(5)	N(27)–Cu(3)–N(23)	94.3(5)
C(12)–N(13)–Cu(2)	114.5(11)	N(31)–Cu(3)–O(19)	87.6(5)
N(17)–Cu(2)–O(10)	165.8(6)	N(31)–Cu(3)–O(22)	106.0(5)
N(17)–Cu(2)–N(13)	97.5(5)	N(31)–Cu(3)–N(23)	152.8(6)
O(20)–Cu(2)–O(10)	91.7(4)	N(31)–Cu(3)–N(27)	93.9(6)
O(20)–Cu(2)–N(13)	167.3(5)		

structure with the atomic numbering scheme is shown in Figure 4. In Table IX the significant bond lengths and angles are given.

The main feature of the trinuclear cation is the presence of a coordinated water molecule in the apical position of the square-pyramidal coordination sphere of the central Cu(2) atom. The metal ion is displaced 0.22 Å from the least-squares basal plane formed by the N(13), N(17), O(10), and O(20) atoms, toward the Ow oxygen atom. No significant tetrahedral distortion was found in this case, but the local geometry of Cu(2) causes a bending of the trinuclear cation, with an angle between the planes of the bridging oxamato groups of 140.5°. Concerning the terminal Cu(II) ions, we again found them in environments that were intermediate between square-pyramidal and trigonal-bipyramidal. If we assume that the former coordination is the leading one, we find the Cu(1) atom 0.21 Å displaced toward the axial position from the basal mean plane formed by the N(1), N(4), N(7), and O(11) atoms, while Cu(2) is only 0.19 Å from the mean plane defined by N(23), N(27), N(31), and O(19). The axial oxygen atoms of the oxamato bridges are 2.40 and 2.37 Å (for O(8) and O(22), respectively) away from the plane.

The Cu–Cu separations within the trinuclear unit are Cu(1)---Cu(2) = 5.303 Å and Cu(2)---Cu(3) = 5.269 Å. The shortest Cu---Cu intermolecular separations are 6.597 and 6.702 Å for Cu(1)---Cu(2)′ (x, $^1/_2-y$, $^1/_2+z$) and Cu(1)---Cu(2) ($^1/_2-x$, $-y$, $^1/_2+z$), respectively.

Magnetic Properties. The susceptibility measurements were carried out in the 300–4.2 K temperature range. The $\chi_M T$ plots versus T are shown in Figure 5 for compounds **1**–**5**. At room

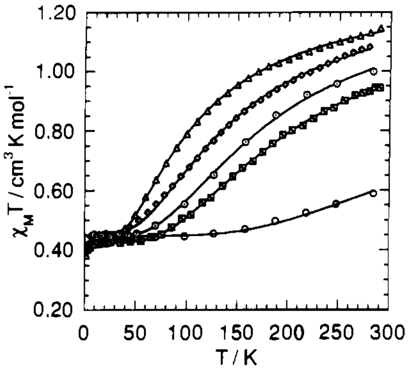

Figure 5. Experimental (points) and calculated (lines) temperature dependences of the product $\chi_M T$ for compounds **1** (○), **2** (▣), **3** (◎), **4** (◇), and **5** (△).

Table X. Least-Squares Values for the Magnetic Parameter Fitting of the Magnetic Susceptibility Data of Compounds **1–5**

	J	g_C	g_T	Θ	10^5R
1	−379	2.10	2.17	−0.36	7.7
2	−172	2.24	2.16	−0.30	2.6
3	−152	2.24	2.20		4.9
4	−117	2.20	2.17		5.1
5	−84	2.16	2.19	−0.27	2.8

temperature $\chi_M T$ values are smaller than expected for three uncoupled Cu(II) ions (1.3 cm^3·mol^{-1}·K) and are equal to 0.59, 0.94, 1.09, 1.14, and 1.16 cm^3·mol^{-1}·K for **1–5**, respectively. The $\chi_M T$ product decreases upon cooling and presents a plateau at low temperature with $\chi_M T$ values equal to 0.44, 0.43, 0.45, 0.45, and 0.43 cm^3·mol^{-1}·K for **1–5**. These values are in the expected range for spin doublet states. At very low temperature, the $\chi_M T$ product of **1**, **2**, and **5** decreases, indicating that an intermolecular antiferromagnetic interaction occurs in these compounds. The experimental data were fitted using the theoretical expression deduced from the following spin Hamiltonian:

$$\hat{H} = -J[\hat{S}_{T1}\hat{S}_C + \hat{S}_C\hat{S}_{T2}] + \beta\vec{H}(g_T[\hat{S}_{T1} + \hat{S}_{T2}] + g_C\hat{S}_C) \quad (1)$$

with T_1 and T_2 being the two terminal Cu(II) ions and C the central one. In this Hamiltonian, the interaction between the terminal ions is assumed to be nil. Using the Van Vleck formula, the susceptibility expression is given as

$$\chi_M = \frac{N\beta^2}{k(T-\Theta)} \times \frac{{}^1/_2\left(\frac{4g_T - g_C}{3}\right)^2 e^{-J/kT} + {}^1/_2 g_C{}^2 + 5\left(\frac{2g_T + g_C}{3}\right)^2 e^{J/kT}}{2\,e^{-J/kT} + 2 + 4\,e^{J/kT}} \quad (2)$$

The Curie–Weiss parameter Θ is introduced to take into account possible intermolecular interaction when necessary. The different g factors of the doublet ground state and the excited doublet and quartet states are given by Bencini and Gatteschi.[16,17] Minimizing $R = \sum[(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2/\sum[(\chi_M T)^{obs}]^2$ by a simplex method leads to the values listed in Table X. For compound **2**, due to the presence of two different trinuclear entities in the unit cell, the J value corresponds to their average.

Electron Paramagnetic Resonance Spectra. The g values obtained from the powder EPR spectra at liquid-nitrogen temperature for compounds **1–5** are summarized in Table XI. No temperature dependence is observed upon warming. The spectrum of **1** presents axial symmetry with $g_\parallel > g_\perp$; the spectra of **2–5** are quasi-isotropic. The magnetic susceptibility data show that, at liquid-nitrogen temperature, the doublet ground state is the most populated for all compounds.

Table XI. g-Values Obtained from the X-Band EPR Spectra of Compounds **1–5** at Liquid-Nitrogen Temperature

	g_1	g_2	g_3	$\langle g \rangle$
1	2.249	2.128	2.096	2.158
2		isotropic		2.150
3		isotropic		2.090
4		isotropic		2.116
5		isotropic		2.106

EPR spectroscopy is generally presented as a molecular probe allowing the determination of both the ground-state symmetry and multiplicity. For trinuclear copper(II) complexes, the **g** tensor of the doublet ground state is related to the individual tensors of the copper ions by[16,17]

$$\mathbf{g} = {}^1/_3[2\mathbf{g}_{T1} - \mathbf{g}_C + 2\mathbf{g}_{T2}] \quad (3)$$

Taking into account the local orientation of the three copper(II) tensors and eq 3, the resulting tensors for the doublet ground states of **2–5** are expected to be weakly anisotropic and of axial symmetry, with $g_\parallel < g_\perp$, the z axis being orthogonal to the Cu(pba)$^{2-}$ plane. For **1** an axial tensor is also expected but with $g_\parallel > g_\perp$. Except for **1**, this feature is not observed and the shapes of the spectra are not compatible with eq 3. To understand the EPR properties of these species, we looked at the single-crystal spectra of **1** and **3**. For **1**, owing to the orthorhombic symmetry, four magnetically nonequivalent centers are expected (two in the *ab*, *bc*, or *ac* planes). For compound **3** two magnetically nonequivalent sites are expected (monoclinic symmetry). In the present cases only one line is observed whatever the orientation of the crystal for **1** and **3**. This indicates that the trinuclear cations are not perfectly isolated from a magnetic viewpoint. Intermolecular interactions are operative and the exchange averaging condition[18–20] is fulfilled:

$$|J^*| > {}^1/_2\beta H|g_a - g_b| \quad (4)$$

J^* being the interaction between two nonequivalent magnetic centers noted a and b. Taking a large value for δg like $\delta g = 0.2$, we can evaluate J^* as 0.015 cm^{-1}, which is undetectable on magnetic susceptibility measurement at 4.2 K. Therefore, an extremely weak value of intermolecular exchange interaction leads to the exchange averaging effect, which is responsible for the isotropic spectrum observed for compound **3**. This is probably the case for compounds **2**, **4**, and **5**. The case of **1** is particularly puzzling: the symmetry of its spectrum is compatible with formula (3), but nevertheless the appearance of the spectrum is due to intermolecular averaging.

More generally, formula (3) indicates that, due to disorientation of the local **g** tensors inside the trinuclear unit, the **g** tensor of the doublet ground state is expected to be less anisotropic than the **g** tensor of mononuclear species. It is well-known that exchange averaging condition are frequently fulfilled for mononuclear copper(II) complexes.[20,21] Therefore, it is highly probable that the intermolecular exchange averaging condition is always fulfilled for trinuclear copper(II) compounds. This shows that special care should be exercised when interpreting powder spectra of trinuclear copper(II) complexes.

Discussion

It is well-known that Hamiltonian (1) is an effective Hamiltonian that does not correspond to the real mechanism of exchange

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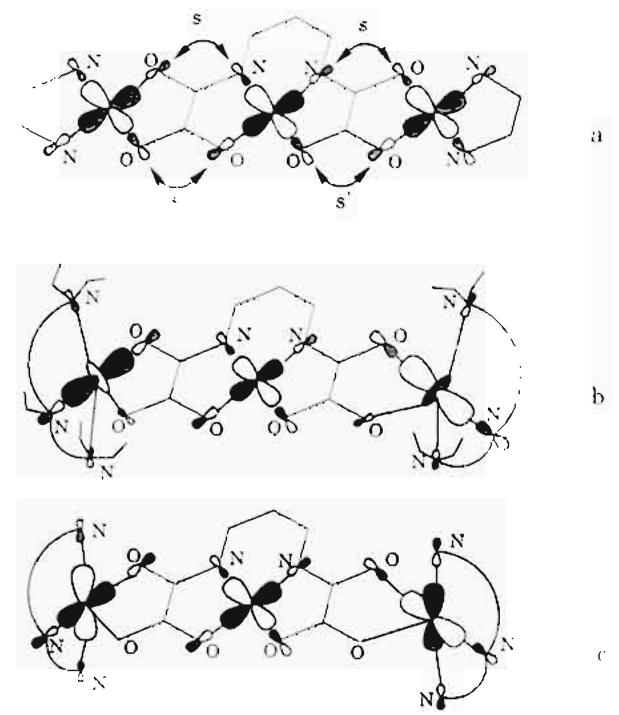


Figure 6. Relative orientations of the magnetic orbitals when they lie (a) all coplanar in square-planar or square-based pyramidal coordinations, (b) in different planes with square-based pyramidal coordination for both Cu(II) terminal ions, or with (c) tbp coordination for both Cu(II) terminal ions.

interaction. For linear trinuclear copper(II) complexes, using a nonorthogonal magnetic orbitals basis, it has been shown that the coupling constant J is expressed as[6c]

$$J = 4tS + 2j - 4kS^2 \tag{5}$$

with $S = \langle a_1(i)|a_2(i)\rangle$, $\alpha_k = \langle a_k(i)|H(i)|\,a_k(i)\rangle$, $\beta = \langle a_1(i)|H(i)|a_2(i)\rangle$, $t = \beta - (\alpha_1 + \alpha_2)/2S$, $k = \langle a_1(i)a_1(j)|1/r_{12}|a_2(i)a_2(j)\rangle$, and $j = \langle a_1(i)a_2(j)|1/r_{12}|a_1(i)a_2(j)\rangle$. The a_k symbols represent the magnetic orbitals. If the terms in S^2 are neglected, this formula leads to

$$J = 4tS + 2j \tag{6}$$

In formula (6), the $4tS$ term is negative and corresponds to the antiferromagnetic contribution of the exchange interaction. On the other hand, the exchange integral k is positive and accounts for the ferromagnetic part of the interaction. For extended bridges like oxamato, the exchange integral k is vanishingly small.[22] Consequently, the variation of the coupling constant J can be understood as refering only to the variation of the first term of formula (5). This term varies approximately as S^2, S being the overlap integral between the magnetic oribitals.

In the series presented here, the coordination around the central copper atoms is either 4 or 4 + 1. Thus, the magnetic orbitals are well described by the antibonding combination of the $d_{x^2-y^2}$ metallic orbitals with the symmetry-adapted molecular orbitals of the oxamato bridge. Concerning the terminal copper atoms, the five compounds can be divided into two groups. The first contains compound **1**, where the environment around the two terminal copper atoms is 4 + 1 and 4 + 2, respectively. Their magnetic orbitals are approximately coplanar with that of the central ion and have $x^2 - y^2$ symmetry. This situation is depicted in Figure 6a. The second group contains the remaining complexes, where the tridentate ammine ligands impose five-coordinated terminal copper atoms. The coordination around these atoms varies between two ideal geometries, trigonal-bipyramidal and square-pyramidal, depending on the bulkiness of the substituent on the nitrogen atoms. Actually, the bulkier the substituents, the closer the geometry is to trigonal-bipyramidal. The two extreme situations are shown in Figure 6b,c. In the square-pyramidal case the terminal magnetic orbitals are located in planes orthogonal to the oxamato bridge. The evolution between the two geometries can be quantified using the τ parameter[23] defined as

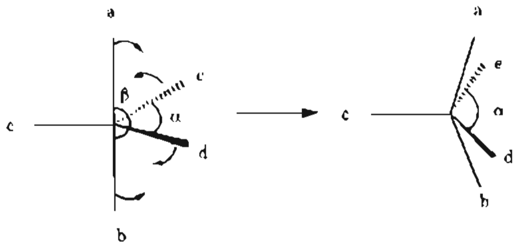
Table XII. Experimental Values of the Geometric τ Parameter for Terminal Copper(II) Atoms in Compounds **2**–**4**[a]

		compound								
		2				**3**		**4**		
	tbp	Cu (1)A	Cu (3)A	Cu (1)B	Cu (3)B	Cu (1)	Cu (3)	Cu (1)	Cu (3)	sbp
τ	1	0.50	0.58	0.74	0.64	0.48	0.54	0.39	0.38	0
$\langle\tau\rangle$	1	0.64				0.51		0.38		0

[a] The average values are also presented and compared with those of the ideal trigonal-bipyramidal and square-based pyramidal geometries (tbp and sbp, respectively).

$$\tau = (\beta - \alpha)/60$$

The angles α and β are defined in the scheme below.



The main factor in the distortion is the variation of the α angle going from a square-pyramid (sp, α = 180°, τ = 0) to trigonal-bipyramid (tbp, α = 120°, τ = 1). In Table XII we have computed the values of the τ parameter for all the different terminal copper atoms in compounds **2**–**4**. The rigidity of the terpy ligand in compound **5** leads us to expect an environment close to square-pyramidal, with a τ factor near 0.25, according to recent literature data.[24]

Having defined the magnetic orbitals on each copper atom, the key point is now to evaluate the overlap between these magnetic orbitals in order to understand the variation of the J parameter along the series. The situation depicted in Figure 6a, which is close to that of compound **1**, shows that the overlap is maximal, leading to a J value of the order of -380 cm^{-1}. In this case, the overlap integral can be approximated as $(s+s') \approx 2s$, where s and s' are defined as the overlap in the amido and the carboxylato moieties, respectively; consequently, J depends on $(s+s')^2 \approx 4s^2$.

When the terminal ligands restrict the geometry in such a way that the magnetic orbitals are not in the same plane or of the same type, the overlap is reduced and the magnitude of the interaction is smaller.

In case b, the two terminal magnetic orbitals are of the z^2 type (tbp, τ = 1) and lie in the plane of the central atom orbital. Taking into account the ratio between the lobes of the d_{z^2} orbital, the overlap could be evaluated as $\sqrt{3}/3(2s + s') \approx s\sqrt{3}$. This leads to a coupling constant proportional to $3s^2$, which is expected to be close to $^3/_4J$. In case c, in contrast, the magnetic orbitals of the $x^2 - y^2$ type lie in planes orthogonal to that of the central copper atom (sp, τ = 0), s' vanishes, and the total overlap is equal

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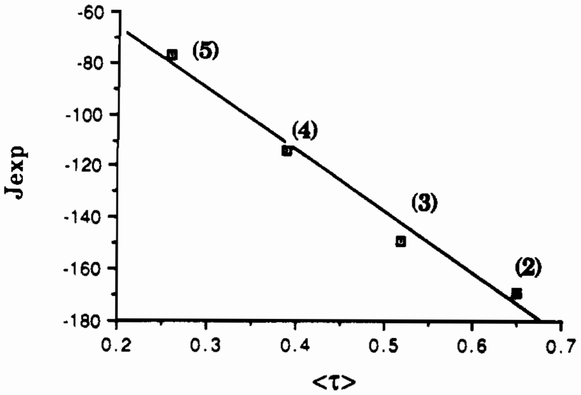

Figure 7. Representation of the experimental J values for compounds **2**–**5** versus the average τ parameters of their terminal copper(II) ions. The expected τ value is plotted for product **5**.

to s. The coupling parameter is then proportional to s^2 and is expected to be close to $J/4$.

Structural data for compounds **2**–**4**, and presumably **5**, present intermediate situations between the two latter cases. Despite the drastic approximation of the model, the J parameter values lie in the expected range and moreover vary in the right way. Figure 7 shows a simple linear relationship between the values of the experimental J parameter and the average values of the experimentally determined distortion parameter τ. This relation confirms that the closer the geometry of the terminal copper(II) ions is to trigonal-bypiramid the higher the coupling constant is.

In this paper, we report the synthesis of five new trinuclear complexes with almost the same intramolecular Cu---Cu distances. However, the magnitude of the magnetic interactions varies within a large range (J = –400, –80 cm^{-1}). These results show that by choosing appropriate terminal ligands, it is possible to tune the exchange interaction between copper(II) ions within trinuclear complexes. This stresses the fact that the mechanism of the exchange interaction is really governed by the magnitude of the overlap between magnetic orbitals, the Cu(II)–Cu(II) distance being only a secondary parameter.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (39 pages). Ordering information is given on any current masthead page.